

Manganese is the key element that activates the enzyme system responsible for splitting the water molecule in the photosynthesis process, and therefore it is ultimately responsible for the presence of oxygen in the atmosphere. In biological systems, especially in animals, Fe is supreme and plays a dominant role, while Mn is secondary and displays some toxicity tendencies. In the oxidation-reduction reactions of soils, however, Fe is second to Mn in importance. Manganese and iron together provide the key to the establishment of the organic mantle, the humified soil top layer that covers the surface of the earth and serves as the nurturing home for the roots of all plants and carbon-recycling microorganisms (Bartlett and James, 1993). Manganese provides O_2 to the poorly ventilated interior soil pores, where Fe^{2+} and complex organic molecules would otherwise tend to remain unoxidized.

There are a number of similarities in the behavior of Fe and Mn in soils and plants. They are as follows:

1. Both Fe and Mn are transition elements and have more than one valency.
2. Both Fe and Mn are soluble in the +2 valency form (Fe^{2+} and Mn^{2+}).
3. Both Fe and Mn are present in soils as oxides, hydroxides, and oxyhydroxides.
4. Compared with the quantities present in soil, both Fe and Mn are taken up by plants in small amounts.
5. Under anaerobic conditions, especially in acidic soils, both Fe and Mn can reach toxicity levels.
6. In acidic soils both Fe and Mn are involved in phosphate retention.
7. While in soils Fe^{2+} (ferrous) and Mn^{2+} (manganous) forms are fairly mobile; both Fe and Mn are immobile in plants.
8. Both Fe and Mn are involved in the process of photosynthesis in plants.
9. Both nutrients can partly substitute for one other plant nutrient. Iron can partially substitute for Mo as the metal cofactor necessary for the functioning of nitrate reductase. Manganese can substitute to some extent for Mg in phosphorylation and group transfer reactions.

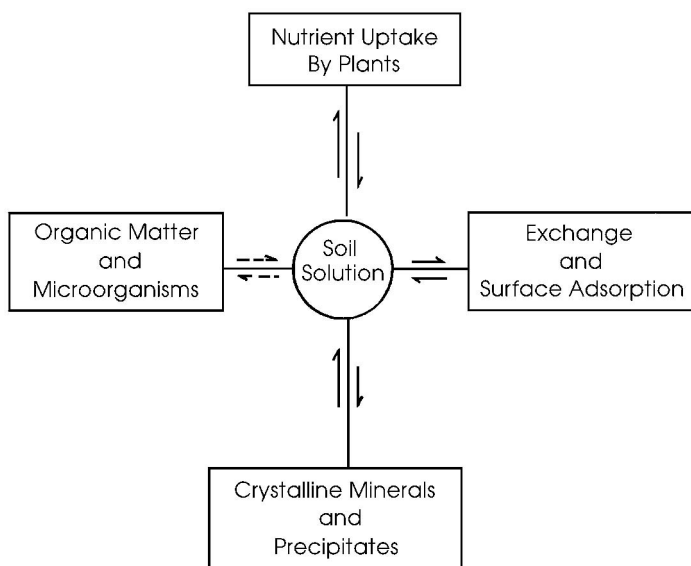


Figure 13.1. Dynamic equilibria for micronutrients occurring in soils. (From Lindsay, 1991. *Micronutrients in Agriculture*, J.J. Mortvedt, F.R. Cox, L.M. Shuman, and R.M. Welch, Eds., pp. 89–112. With permission of SSSA.)

10. Both Fe and Mn are involved in imparting specific color(s) to the soils, providing the base for such names as terra rosa, krasnozems, red earths, yellow earths, etc.

13.1. AMOUNTS AND FORMS OF IRON AND MANGANESE IN SOIL

Iron comprises about 50 g kg^{-1} (5%), while Mn is present at about 1 g kg^{-1} (0.1%) of the earth's crust. The amounts of Fe and Mn in a soil depend upon the kind and degree of weathering the parent material has undergone during soil formation. The amounts of these elements are greatest in highly weathered oxisols and ultisols.

As already indicated, Fe and Mn are mostly present as oxides, hydroxides, and oxyhydroxides, which have been discussed in [Chapter 4](#). Small amounts of Fe and Mn may be present as chlorides, sulfates, and carbonates.

The relationship existing between different micronutrient pools (this applies to Fe as well) is shown in Figure 13.1.

13.2. SOIL SOLUTION IRON AND MANGANESE

Both Fe and Mn must exist in their +2 valence form to be soluble in soil solution and taken up by plants. Diffusion is the main process by which Fe

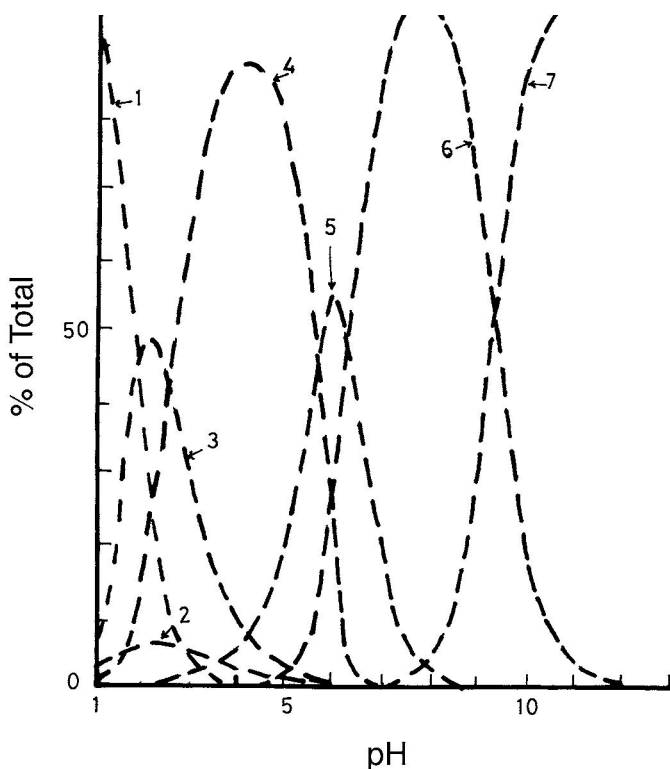


Figure 13.2. Relative concentrations of the principal series in a 0.1 M Fe(III) solution. 1 = Fe^{3+} , 2 = FeOH^{2+} ; 3 = $\text{Fe}_2(\text{OH})_2^{4+}$; 4 = $\text{Fe}_3(\text{OH})_4^{5+}$; 5 = $\text{Fe}(\text{OH})_2^+$; 6 = $\text{Fe}(\text{OH})_3$; 7 = $\text{Fe}(\text{OH})_4^{2-}$. (From Baes and Mesmer, 1976. *The Hydrolysis of Cations*. With permission of John Wiley & Sons.)

and Mn ions are made available for uptake by plants. The other processes involved in uptake of Fe^{2+} and Mn^{2+} by plants are mass flow and root interception. Chelation by fulvic and other low-molecular-weight humic acids produced on the decomposition of soil organic matter plays an important role in solubilizing Fe and keeping it in soil solution.

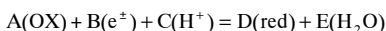
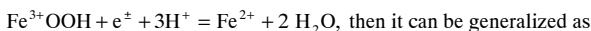
In aqueous solution Fe^{3+} is surrounded by six molecules of water, that is as $\text{Fe}(\text{H}_2\text{O})_6^{3+}$. Increasing pH removes H^+ from the coordinated water and gives rise to various hydrolysis products as shown in Figure 13.2. The hydrolysis species are important in soils because they increase total soluble Fe, which determines transport from soil to plant roots, a rate-limiting step in Fe nutrition of plants.

pH has a significant influence on the solubility of Fe, which is minimum in the pH range 7.4 to 8.5, characteristic of calcareous soils. This would explain why Fe deficiency is most prevalent in calcareous alkaline soils (Loeppert and Hallmark, 1985). A soil solution at pH 8.0 in equilibrium with soil Fe contains only $10^{-21.3}$ M Fe^{3+} , whereas the total soluble Fe components also consists of

$10^{-10.4} M \text{ Fe (OH)}^0$, $10^{-10.9} M \text{ Fe (OH)}^-$, and $10^{-11.0} M \text{ Fe (OH)}_2^+$, giving a total soluble Fe of $10^{-10.20} M$ (Lindsay, 1988). This level of Fe is much below that needed to supply adequate Fe to most crops. Most plants need in excess of $10^{-8} M$ of soluble Fe in the soil solution to meet their nutritional needs (Schwab and Lindsay, 1989). Inorganic Fe^{+3} can maintain this level of soluble Fe only in soils with pH below 5.5 to 6. At higher soil pH levels, chelation by natural (organic) or synthetic chelates or reduction to Fe^{+2} is necessary to raise the solubility of Fe in soils to acceptable levels (Lindsay, 1991).

Because both Fe and Mn are transition metals and change valence while undergoing oxidation-reduction reactions, recently the redox parameter $(\text{pe} + \text{pH})^*$ has been used to quantify the ionic species present in a solution (Figure 13.3). A value of zero for $\text{pe} + \text{pH}$ corresponds to the redox level imposed by one atmosphere of H_2 (g) in equilibrium with an aqueous system, while an aqueous system in equilibrium with one atmosphere of O_2 (g) has a $\text{pe} + \text{pH}$ value of 20.8 (Lindsay, 1991). Most well-aerated soils have a redox $(\text{pe} + \text{pH})$ value of 12 to 16, while submerged paddy soils have a value of 4.0. Figure 13.3 shows that if soil-Fe controls Fe solubility, $\text{pe} + \text{pH}$ would have to be <10 (at pH 7) or 8 (at pH 8) in order for Fe^{2+} activity to exceed the $10^{-8} M$ level required by most crop plants.

* If an oxidation-reduction is written as



where A, B, C, D, and E are reaction coefficients for oxidized species (OX), electron (e^-), proton (H^+), reduced species (red), and water, respectively. This can be expressed as:

$$\text{K} = (\text{red})^{\text{D}} (\text{H}_2\text{O})^{\text{E}} / (\text{OX})^{\text{A}} (\text{e}^{\pm})^{\text{B}} (\text{H}^+)^{\text{C}}$$

where K is the equilibrium constant. Taking the log of both sides of this equation we obtain

$$\log \text{K} = \log(\text{red})^{\text{D}} / \log(\text{OX})^{\text{A}} + \log \frac{1}{(\text{e}^{\pm})^{\text{B}}} + \log \frac{1}{(\text{H}^+)^{\text{C}}}$$

$$\text{or } \log \text{K} = \text{D } \log(\text{red}) \pm \text{A } \log(\text{OX}) + \text{B(pe)} + \text{C(pH)}$$

where pe and pH are defined as $-\log$ of electron activity and hydrogen ion activity, respectively.

For one-electronic transfer ($\text{B}=1$) coupled with one-proton consumption ($\text{C}=1$) and when $\text{D} = \text{A}$ and $(\text{red}) = (\text{OX})$,

$$\text{pe} + \text{pH} = \log \text{K}$$

For details see Bartlett and James, (1993).

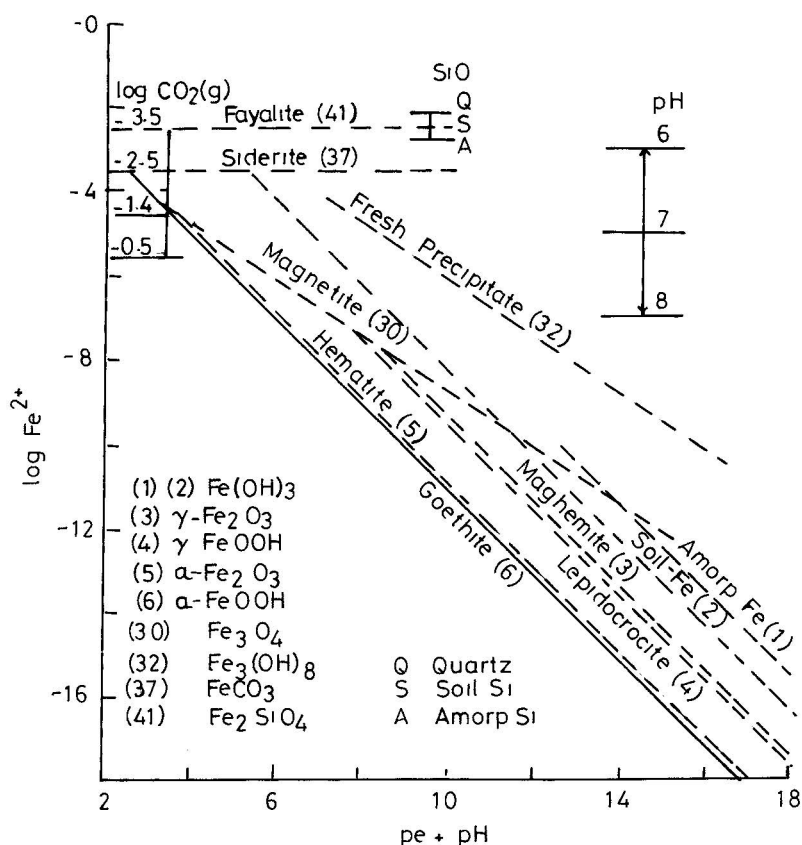


Figure 13.3. Effect of redox level, CO_2 (g), and silica on Fe^{2+} maintained by various Fe minerals at pH 7, showing shifts for other pH values. (From Lindsay, 1991. *Micronutrients in Agriculture*, J.J. Mortvedt, F.R. Cox, L.M. Shuman, and R.M. Welch, Eds. pp. 89–112. With permission of SSSA.)

The availability of Fe in soils therefore very much depends upon the availability of electrons. Thus the release of electrons near actively absorbing roots is considered a major mechanism by which Fe-stressed plants are able to increase the solubility and availability of Fe to meet their nutritional needs (Schwab and Lindsay, 1989). In addition to the release of electrons, plant roots also produce other Fe-reducing compounds and accumulate organic acids such as citrate to make soil-Fe more readily available to them. Monocots usually do not produce or excrete as much reducing compounds or organic acids as dicots. Even in the same species there are considerable differences between the cultivars, and breeding for Fe-deficiency-tolerant cultivars is being attempted (Pierson et al., 1984).

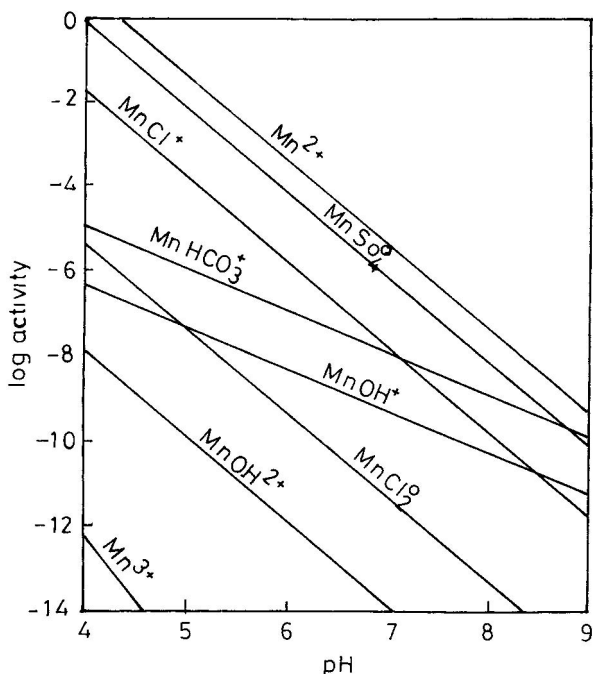


Figure 13.4. Solution species of Mn in equilibrium with manganite and pyrolusite at $p_e + \text{pH } 16.1$, when Cl^- and SO_4^{2-} are at 10^{-3} M and CO_2 is at $10^{-4.52} \text{ MPa}$ ($10^{-3.52} \text{ atm}$). (From Lindsay, 1991. *Micronutrients in Agriculture*, J.J. Mortvedt, F.R. Cox, L.M. Shuman, and R.M. Welch, Eds. pp. 89–112. With permission of SSSA.)

In contrast to Fe, there are not many hydroxylated species of Mn in soil solution; the most abundant soil solution species is Mn^{2+} (Figure 13.4). The important ion pairs are MnSO_4 and MnCl^+ at pH values below 7, and only at pH values above 8 would the ion pairs MnOH^+ and MnHCO_3^+ assume importance. A tenfold increase in CO_2 (g) would raise the MnHCO_3^+ species by one log unit. In acid soils, as well as in submerged paddy soils, Mn solubility can increase to the toxicity level. Liming these soils raises pH and eliminates Mn toxicity.

13.3. FACTORS AFFECTING IRON AND MANGANESE AVAILABILITY

In addition to pH and soil water or aeration as measured by redox, soil organic matter and interactions with other ions in soil solution also affect the availability of Fe and Mn.

13.3.1. Organic Matter

Organic materials added to soil produce chelating agents such as simple aliphatic acids, hydroxamate siderophores, phenols and phenolic acids, complex polymeric phenols, and components of stable humus such as humic and fulvic acids (Stevenson, 1991). These chelating agents make more Fe and Mn available to plants. Hydroxamate siderophores play an important role in the Fe nutrition of plants growing on calcareous soils. These substances are produced by soil bacteria and fungi, including ectomycorrhizal fungi (Powell et al., 1980; Jukrevitch et al., 1988). Mandal (1961) found that the application of rice straw to paddy fields increased soil solution Fe^{2+} concentration from 0 to 132 mg L^{-1} and exchangeable Fe^{2+} from 20 to 200 mg kg^{-1} soil after 4 weeks of submergence. Similarly, the application of 10% peat moss along with 54 mg kg^{-1} Mn to Norfolk sandy loam increased acid-extractable Mn from 48 to 53.9 mg kg^{-1} (Sanchez et al., 1959).

13.3.2. Interaction with Other Nutrients

Excesses of essential nutrients such as P, Cu, Zn, and Mo adversely affect the availability of Fe. Phosphorus application at high rates aggravates Fe and Mn deficiency through some poorly defined inactivation reaction.

Application of NH_4^+ -containing or producing fertilizers are likely to result in less Fe or Mn deficiency, while application of NO_3^- -containing fertilizers is likely to enhance the deficiency of Fe and Mn. Neutral chloride-containing salts when applied also increase Mn availability.

13.4. SOIL TESTS FOR IRON AND MANGANESE

Because only a small fraction of Fe and Mn present in soil is available for plant growth, a number of chemical extracts have been evaluated for estimating available soil Fe and Mn concentrations. These are listed in [Table 13.1](#). As expected, critical values for different soil tests and different crops using the same soil test will differ. The predictability of Fe and Mn soil tests (or for any other nutrient) will thus depend much upon the thoroughness with which soil test results are correlated with greenhouse or field crop response data.

Efforts have been made to use a common chemical extractant for a number of micronutrients. For example, the DTPA-TEA soil test was developed (Lindsay and Norvell, 1978) for simultaneous estimation of available Fe, Mn, Cu, and Zn in near-neutral and calcareous soils.

Attempts have also been made to fractionate soil Mn forms such as readily soluble Mn, weakly adsorbed Mn, carbonate bound Mn (calcareous soils), specifically adsorbed Mn (noncalcareous soils), and oxide-Mn (Warden and Reisenauer, 1991). Whether such a detailed study will help predict crop responses to Mn fertilization is yet to be seen.

Table 13.1 Critical Levels of Fe and Mn Soil Tests

| Crop | Soils | Extractant | Critical level (mg element kg ⁻¹ soil) | |
|---------|--|--|--|----------|
| | | | Fe | |
| Sorghum | 35 calcareous soils | DPTA-TEA | 4.5 | |
| Sorghum | 40 soils; 35 calcareous and 5 noncalcareous | NH ₄ HCO ₃ -DTPA | 4.8 | |
| Mn | | | | |
| Soybean | 25 soils; pH 5.7–7.4 | 0.033 M H ₃ PO ₄ 1 M NH ₄ H ₂ PO ₄ | 20 | |
| Soybean | 17 soils; pH 5.2–7.1 | Mehlich I | 5.2 | (pH 6.0) |
| | 30 soils; pH 5.1–6.9 | Mehlich I | 4.6 | (pH 6.0) |
| | 38 soils; pH 5.5–7.1 | Mehlich I | 4.7 | (pH 6.0) |
| Soybean | 2 soils; pH 6.2–7.0 | DPTA-TEA | 0.22 | |
| | | NH ₄ HCO ₃ -DTPA | 0.40 | |
| Corn | 1 soil; pH 6.4–7.2 | Mehlich III | 3 | (pH 6.4) |

Adapted from Martens and Lindsay (1990).

Crops differ in their sensitivity to Fe and Mn. Their classification as sensitive, moderately tolerant, and tolerant is shown in [Table 13.2](#) for Fe and [Table 13.3](#) for Mn (Mortvedt, 1980).

13.5. DEFICIENCY SYMPTOMS OF IRON AND MANGANESE

Iron is an immobile nutrient in plants. Therefore its deficiency symptoms show up first in the young leaves of plants. Because 90% of the iron in leaves occurs in chloroplasts and mitochondria, deficiency of Fe results in loss of greenness (chlorophyll) in plants; leaves turn pale green and develop interveinal chlorosis. In severe deficiency the young leaves turn entirely white ([Figure 13.5](#)). Such symptoms are distinctly seen in sorghum, especially when growing on neutral to alkaline soils. Sorghum is an excellent indicator plant for Fe deficiency. Rice nurseries on neutral to alkaline soils and direct-seeded rice crops in early growth stages on similar soils may also show similar symptoms, that is, patches of plants with white young leaves. Iron deficiency of soybeans has become quite common in the western Corn Belt of the United States, but the severity of the deficiency varies with variety or cultivar. Iron deficiency is also reported in citrus orchards and blueberry fields. These deficiency symptoms are often referred to as “iron chlorosis.”

Manganese is also an immobile nutrient in plants, and deficiency symptoms show up in younger leaves as in the case of Fe. In some wide-leaved plants such as corn or soybean ([Figure 13.6](#)), interveinal chlorosis, similar to

Table 13.2 Sensitivity of Crops to Low Levels of Available Iron in Soil^a

| Sensitive | Moderately tolerant | Tolerant |
|------------------|----------------------------|-----------------|
| Berries | Alfalfa | Alfalfa |
| Citrus | Barley | Barley |
| Field beans | Corn | Corn |
| Flax | Cotton | Cotton |
| Forage sorghum | Field beans | Flax |
| Fruit trees | Field peas | Grasses |
| Grain sorghum | Flax | Millet |
| Grapes | Forage legumes | Oats |
| Mint | Fruit trees | Potatoes |
| Ornamentals | Grain sorghum | Rice |
| Peanuts | Grasses | Soybeans |
| Soybeans | Oats | Sugar beets |
| Sudangrass | Orchard grass | Vegetables |
| Vegetables | Ornamentals | Wheat |
| Walnuts | Rice | |
| | Soybeans | |
| | Vegetables | |
| | Wheat | |

^a Some crops are listed under two or three categories because of variations in soil and growing conditions and the different responses of varieties of a given crop. (From Mortvedt, 1980. *Farm Chem.* 143(12):43. With permission of Meister Publishing Co., Willoughby, OH.)

that in the case of Fe-deficiency, is seen. In other crops symptoms are different and have been described under specific terms such as gray speck of oats, marsh spot of peas, and speckled yellow of sugar beets.

13.6. TOXICITY SYMPTOMS OF IRON AND MANGANESE

Acid soils having large amounts of Mn may result in Mn toxicity in plants. Crinkle leaf of cotton observed on highly acid ultisols in the southern United States is due to Mn toxicity (Figure 13.7). Other crops such as soybeans, tobacco, and canola on such soils may also show Mn toxicity symptoms. Mn toxicity is also reported from rice paddies in acidic soils. On such soils Fe-toxicity may also occur.

13.7. IRON AND MANGANESE FERTILIZERS

Soil application of Fe fertilizer is of limited help in rectifying an iron deficiency because applied Fe²⁺ is rapidly oxidized. Foliar application to field

Table 13.3 Sensitivity of Crops to Low Levels of Available Manganese in Soil^a

| Sensitive | Moderately tolerant | Tolerant |
|------------------|----------------------------|-----------------|
| Alfalfa | Barley | Barley |
| Citrus | Corn | Corn |
| Fruit trees | Cotton | Cotton |
| Oats | Field beans | Field beans |
| Onions | Fruit trees | Fruit trees |
| Potatoes | Oats | Rice |
| Soybeans | Potatoes | Rye |
| Sugar beets | Rice | Soybeans |
| Wheat | Rye | Vegetables |
| | Soybeans | Wheat |
| | Vegetables | |
| | Wheat | |

^a Some crops are listed under two or three categories because of variation in soil and growing conditions and different responses of varieties of a given crop. (From Mortvedt, 1980. *Farm Chem.* 143(12):43. With permission of Meister Publishing Co., Willoughby, OH.)

crops and injection of Fe^{2+} -salts directly into trunks and limbs of fruit trees is preferred. In field crops a single application or several spray applications (at weekly or fortnightly intervals) of 2 to 3% solution of ferrous sulfate (650 to 700 L ha⁻¹) is generally required. A list of some iron fertilizers is given in [Table 13.4](#). Other than ferrous sulfate, synthetic iron chelates are quite popular. Iron chelates can be applied to soils; HEDTA chelates are good for acidic soils, EDTA chelates for neutral soils, and EDDHA chelates for alkaline soils.

Manganese fertilizers ([Table 13.5](#)) can be applied to the soil or directly to the crop as a foliar spray. Soil application of manganese sulfate may range from 5 to 25 kg ha⁻¹, depending upon the soil and crop. For foliar application generally a 0.2 to 0.5% solution of manganese sulfate is used.

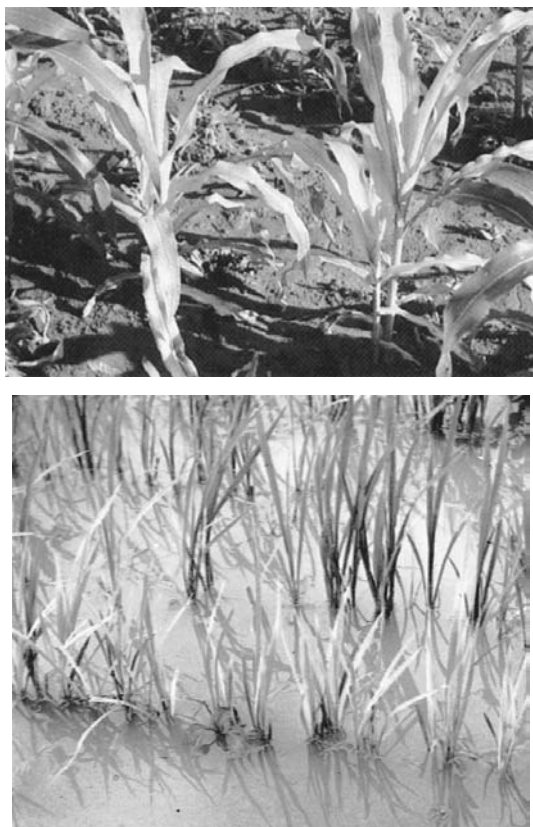


Figure 13.5. Iron deficiency in maize (top) and rice (bottom). (From Yoshida, 1981. *Fundamentals of Rice Crop Science*, p. 269. With permission of International Rice Research Institute, Los Bancos, Philippines.) See Plate 5 following p. 170.



Figure 13.6. Manganese deficiency in maize. (From *Corn Field Manual*, J.R. Simplot Company Mineral & Chemical Division, Pocatello, ID, ©1984. With permission.) See Plate 6.



Figure 13.7. Iron toxicity in rice. (From Yoshida, 1981. *Fundamentals of Rice Crop Science*, p. 269. With permission of International Rice Research Institute, Los Baños, Philippines.) See Plate 7 following p. 170.

Table 13.4 Iron Fertilizers

| Source | Formula | Percent Fe (approx.) |
|-----------------------------|--|----------------------|
| Ferrous sulfate | $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ | 19 |
| Ferric sulfate | $\text{Fe}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ | 23 |
| Ferrous oxide | FeO | 77 |
| Ferric oxide | Fe_2O_3 | 69 |
| Ferrous ammonium phosphate | $\text{Fe}(\text{NH}_4)\text{PO}_4 \cdot \text{H}_2\text{O}$ | 29 |
| Ferrous ammonium sulfate | $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ | 14 |
| Iron frits | Varies | Varies |
| Iron ammonium polyphosphate | $\text{Fe}(\text{NH}_4)\text{PO}_4 \cdot \text{H}_2\text{O}$ | 22 |
| Iron-sul | Mixture $\text{FeO}(\text{OH})$, $\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$, FeS_2 , and CuFeS_2 | 20 |
| Iron chelates | NaFeEDTA | 5–14 |
| | NaFeHEDTA | 5–9 |
| | NaFeEDDHA | 6 |
| | NaFeDTPA | 10 |
| Iron polyflavonoids | — | 9–10 |
| Iron ligninsulfonates | — | 5–8 |
| Iron methoxyphenylpropane | FeMPP | 5 |

From Murphy and Walsh, 1972. *Micronutrients in Agriculture*, J.J. Mortvedt, P.M. Giordano, and W.L. Lindsay, Eds. pp. 347–387. With permission of the Soil Science Society of America, Madison, WI.

Table 13.5 Manganese Fertilizers

| Source | Formula | Percent Fe (approx.) |
|--------------------------------|--|----------------------|
| Manganese sulfate | $\text{MnSO}_4 \cdot 4 \text{H}_2\text{O}$ | 26–28 |
| Manganous oxide | MnO | 41–68 |
| Manganese carbonate | MnCO_3 | 31 |
| Manganese chloride | MnCl_2 | 17 |
| Manganese oxide | MnO_2 | 63 |
| Manganese frits | Fritted glass | 10–25 |
| Natural organic complexes | — | 5–9 |
| Synthetic chelates | MnEDTA | 5–12 |
| Manganese methoxyphenylpropane | MnMPP | 10–12 |

From Murphy and Walsh, 1972. *Micronutrients in Agriculture*, J.J. Mortvedt, P.M. Giordano, and W.L. Lindsay, Eds. pp. 347–387. With permission of the Soil Science Society of America, Madison, WI.

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